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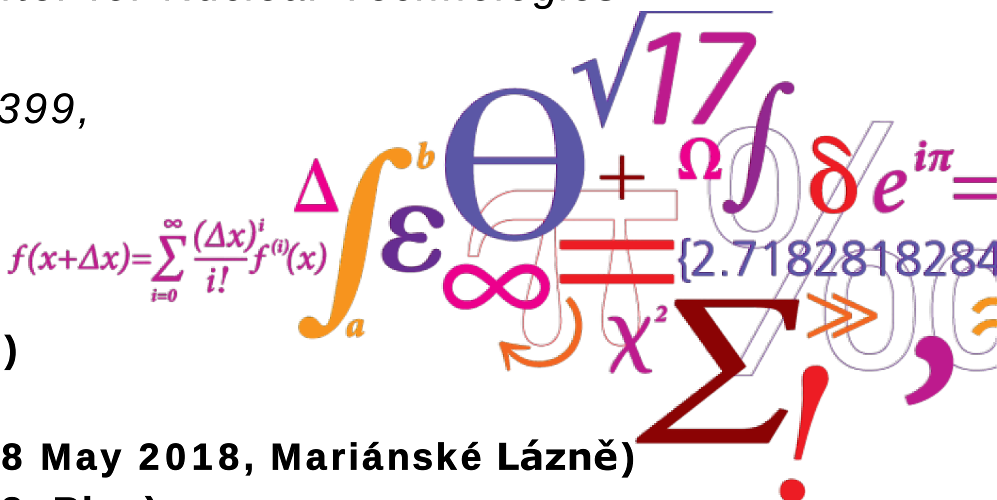
Determination of ^{93}Mo (and ^{94}Nb) in nuclear decommissioning waste from a nuclear reactor

Szabolcs Osváth, Xiaolin Hou, Per Roos, Jixin Qiao, Nikola Marković

Technical University of Denmark, Center for Nuclear Technologies (DTU Nutech)

DTU Risø Campus, Frederiksborgvej 399, 4000 Roskilde, Denmark



RAS academic meeting (23 April 2018)

Nutech meeting (26 April 2018)

18th Radiochemical Conference (13-18 May 2018, Mariánské Lázně)

NKS RadWorkshop (8-12 October 2018, Risø)

A short introduction

- DTU Nutech (Technical University of Denmark, Center for Nuclear Technologies) is the Danish competence center for nuclear technologies.
- The 3 former Danish research reactors were on the campus.
- DTU Nutech (1956-2006 called Risø) has long-term experience on radiochemical analyses of (among others) nuclear waste, especially decommissioning waste.
- ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{93}Mo, ^{93}Zr, ^{94}Nb, ^{99}Tc, ^{129}I, ^{210}Po, ^{210}Pb, ^{226}Ra, ^{237}Np, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, ^{244}Cm; ^{60}Co, ^{152}Eu, ^{154}Eu, ^{134}Cs, ^{137}Cs.

Samples

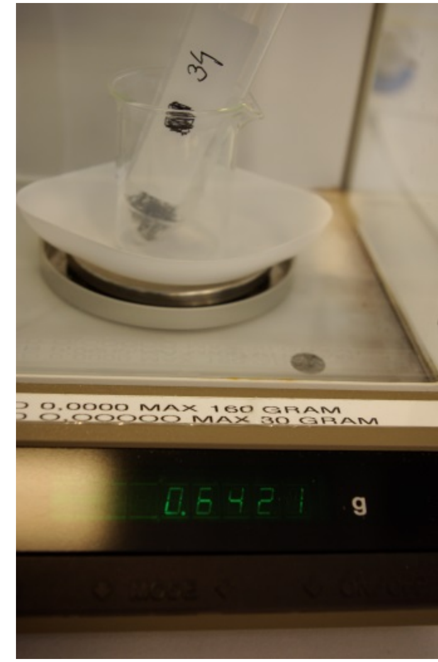
- Metals from a NPP (under decommissioning)
  Main radioactive component: ^{60}Co (≈ kBq-MBq)

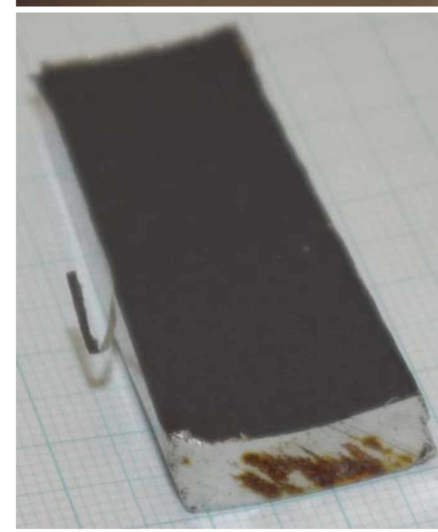
  – Induced activity samples
    Small pieces, irradiated by neutrons
    Activation products

  – Surface layer activity samples
    Big pieces, contacted with primary water
    Corrosion products

- Model sample (for method development):
  NIST Standard Reference Material 123c
  (Cr-Ni-Nb Stainless Steel; AISI 348)

Metal	m / m %
Fe	the rest (68.52%)
Cr	17.40%
Ni	11.34%
Mn	1.75%
Nb	0.65%
Mo	0.22%
Co	0.12%





Goal

- To develop a new method for determination of ^{93}Mo and ^{94}Nb in nuclear power plant decommissioning wastes

^{93}Mo

- $t_{1/2}$ = $(4.0 \pm 0.8) \times 10^3$ years
- Electron capture
- Possibilities for detection:
  - X-ray spectrometry: 16.5 keV (62%) and 18.6 keV (9%) – K_α and K_β lines of Nb
  - LSC: Auger-electrons
  - MS: presence of ^{nat}Mo (abundance sensitivity of ^{92}Mo (15%) and ^{94}Mo (9%))

^{94}Nb

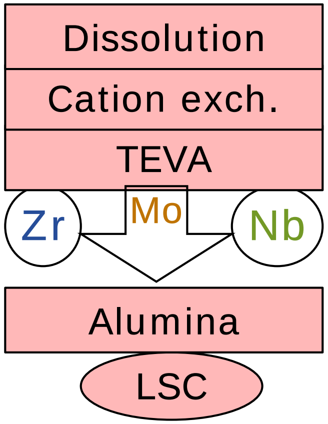
- $t_{1/2}$ = 2.0×10^4 years
- β^-–γ emitter ($E_{\beta,\max}$ = 470 keV)
- Detection by gamma-spectrometry:

  703 keV (98%) and 871 keV (100%)

- Radiochemical separation is needed before measurement!
  - $^{93}Mo/^{60}Co \approx 10^{-5} – 10^{-3}$
  - $^{93}Mo/^{93m}Nb \approx 10^{-5} - 10^{2}$
  - $^{94}Nb/^{60}Co \approx 10^{-5} – 10^{-3}$

  (activity ratios in our samples)

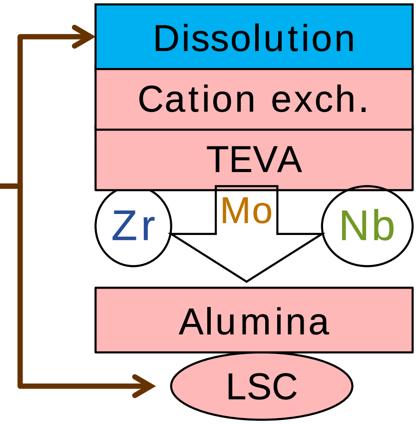
Overview of our method



- Dissolution
- Combined chromatographic separation
  - Cation exchange
  - TEVA
  - Alumina
- Measurements

Detection techniques used in method development:

- Gamma-spectrometry: ^{60}Co, ^{94}Nb, ^{125}Sb; ^{99m}Tc
- ICP-OES: stable elements (Fe, Cr, Ni, Mn, Mo, Nb, Zr)
  - Interferences
  - Extra problem: elimination of HF by dilution, evaporation or complexation (H_3BO_3)



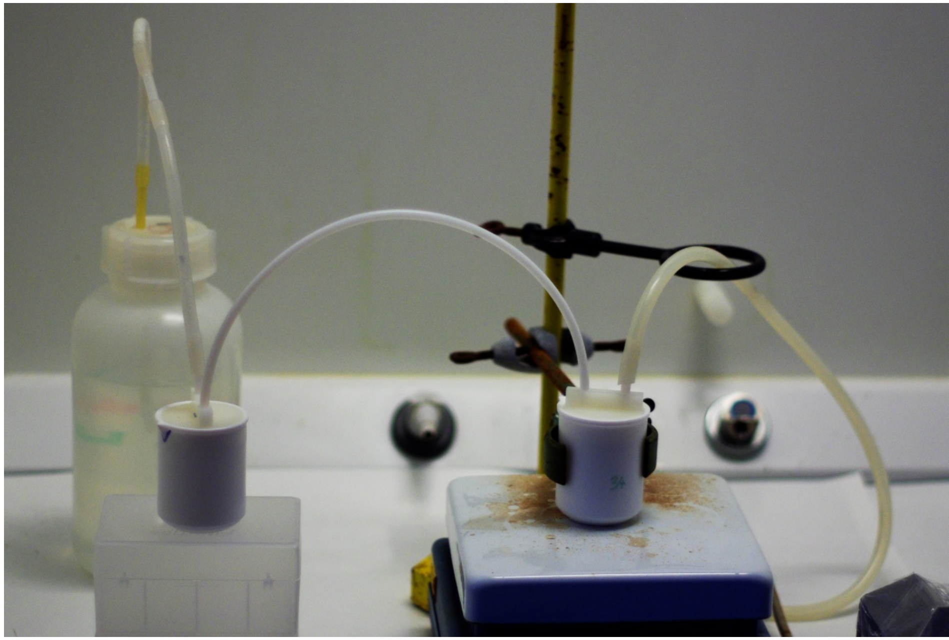
Dissolution

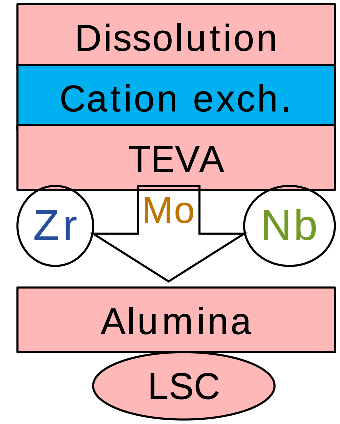
- Surface samples: “leaching” of the activity from the surface
- Induced samples: direct dissolution

- Addition of carriers (stable Mo and Nb)
  - ICP-OEC measurement of aliquots taken before and after separation → Recovery

- Dissolution and repeated evaporation using aqua regia (68% HNO_3 + 36% HCl) and 40% HF
  - Oxidation to MoO_4^{2-} (+VI, crucial)
  - Green solution: Cr^{3+}

- Dissolution in 0.1 M HF
- Dilution until 0.02 M HF





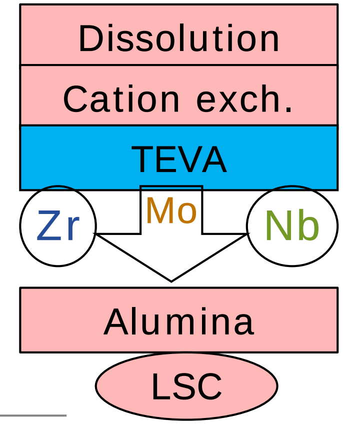
1. column: Cation exchange resin. Getting rid of the matrix

Load & rinse:
0.02 M HF
(lower *c* → higher DF)

Retained: cations
(majority of the activity)
$^{54}Mn^{n+}$, $^{55}Fe^{3+}$, $^{60}Co^{2+}$,
$^{59}Ni^{2+}$, $^{63}Ni^{2+}$, $^{65}Zn^{2+}$, Cr^{3+}

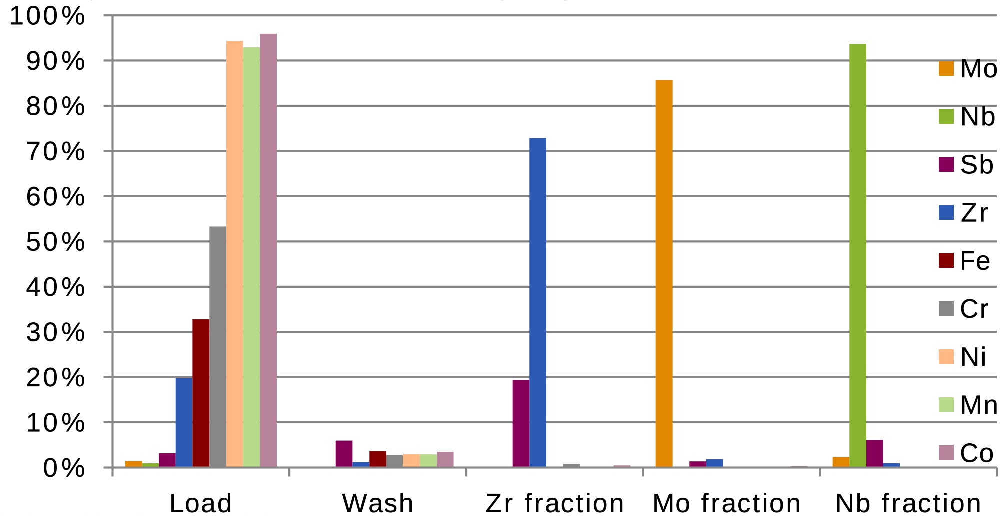
Pass through: anions
^{93}Zr: ZrF_6^{2-}
^{125}Sb: SbF_6^{-}
^{99}Tc: TcO_4^{-}
^{93m}Nb and ^{94}Nb: NbF_6^{-}, $NbOF_5^{2-}$
^{93}Mo: $MoO_2F_3^{-}$, $[MoO_2F_4]^{2-}$, MoF_7^{-}, $MoOF_5^{-}$
CrO_4^{2-} (When applying reducing agents, the Mo recovery is reduced as well.)

2. column: TEVA® resin. Separation of anions

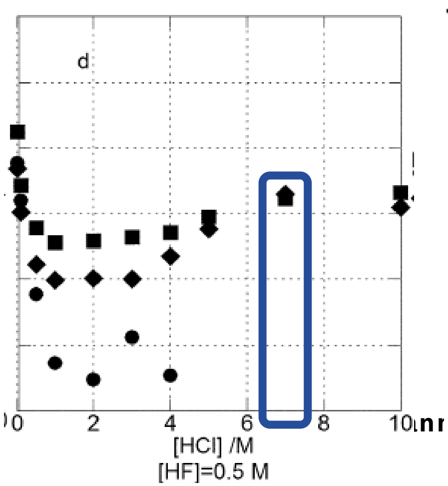


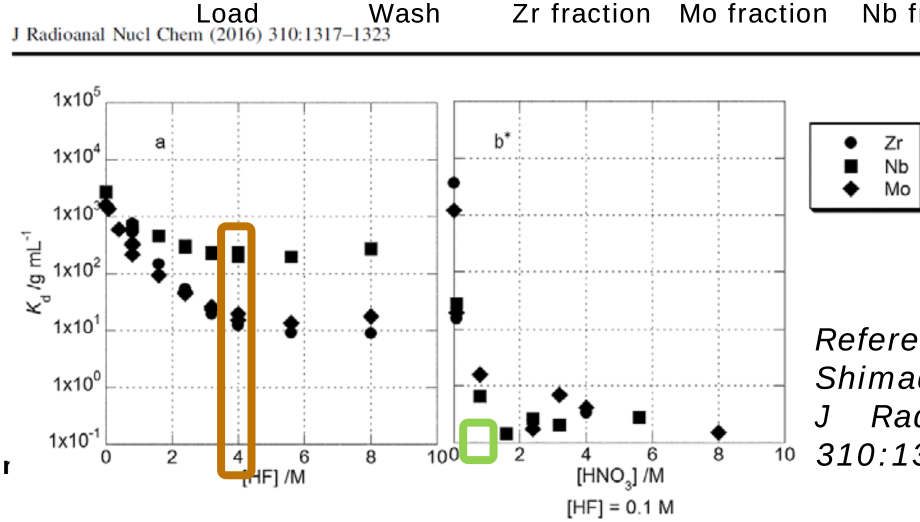
- Based on a quaternary ammonium salt
  (TrisKem product, very similar to anion exchangers)

- Load & rinse: 0.02 M HF
- **Zr strip**:
  5 mL 7 M HCl/0.5 M HF
- **Mo strip**: 12 mL 4 M HF
- **Nb stip**: 10 mL 1 M HNO_3



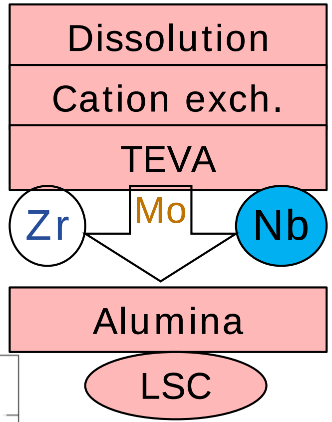
40 mm column 3 mL fractions			
	Zr	Mo	Nb
1.	104%	59%	91%
2.	2%	7%	0.2%
3.	0%	2%	0.1%
4.	0%	1%	-
5.	0% + 1% Nb	1% + 1% Nb	-

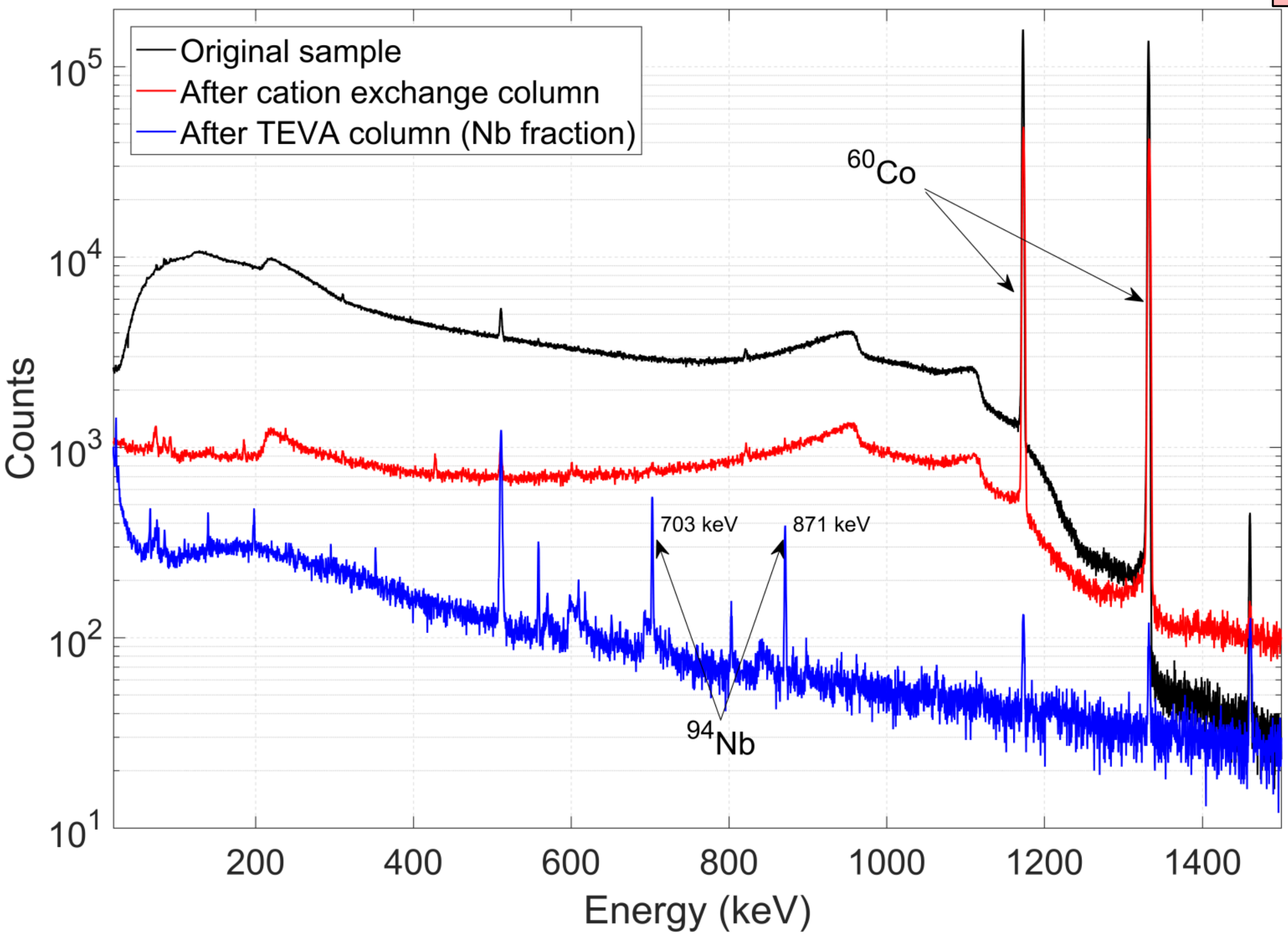




Reference:
Shimada & Kameo (2016)
J Radioanal Nucl Chem
310:1317-1323

Measurement of ^{94}Nb using HPGe





10^5 Bq ^{60}Co

< 70 Bq ^{94}Nb

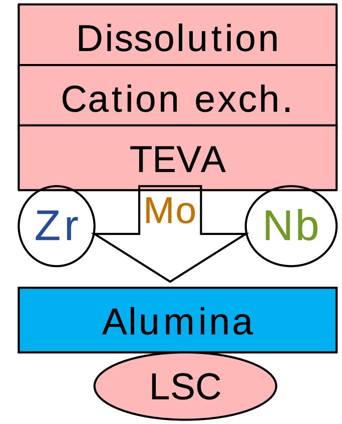
2×10^2 Bq ^{60}Co

< 0.2 Bq ^{94}Nb

10^{-1} Bq ^{60}Co

0.2 Bq ^{94}Nb (MDA = 0.04 Bq)

3. column: Alumina (Al_2O_3). Purification of Mo



- Widely applied for $^{99m}Tc/^{99}Mo$ separation in "technogenerator"s (using HNO_3 media)
- But practically no information is available about usage of HF media

- Load & rinse: 1 M HNO_3
- Wash: 0.1 M HNO_3
  H_2O
  0.01 M NH_3
- Mo strip: 1:1 NH_3

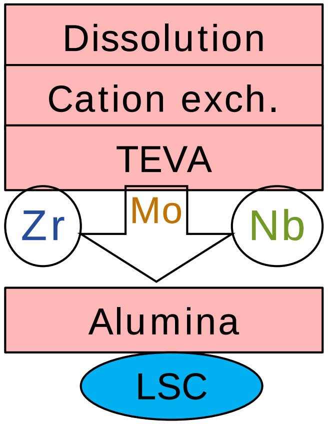
Other metals pass mainly through

- Load & rinse: ≤0.1 M HF
- Wash:
  H_2O
  0.01 M NH_3
- Mo strip: 1:1 NH_3

Other metals are retained

- In general, results are similar
- Higher *c* of NH_3 → more effective elution of Mo (no contaminants were fould)

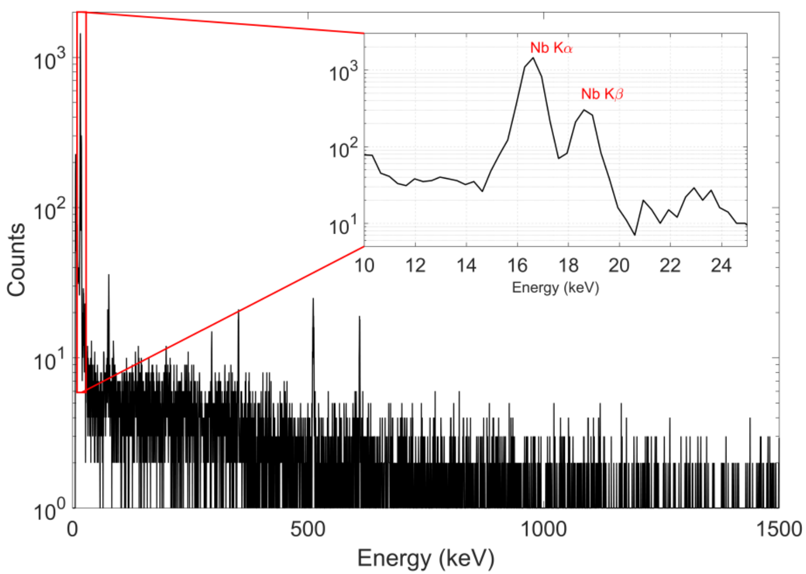
Reference:
Bernhard (1994)
J Radioanal Nucl Chem 177(2):321-325



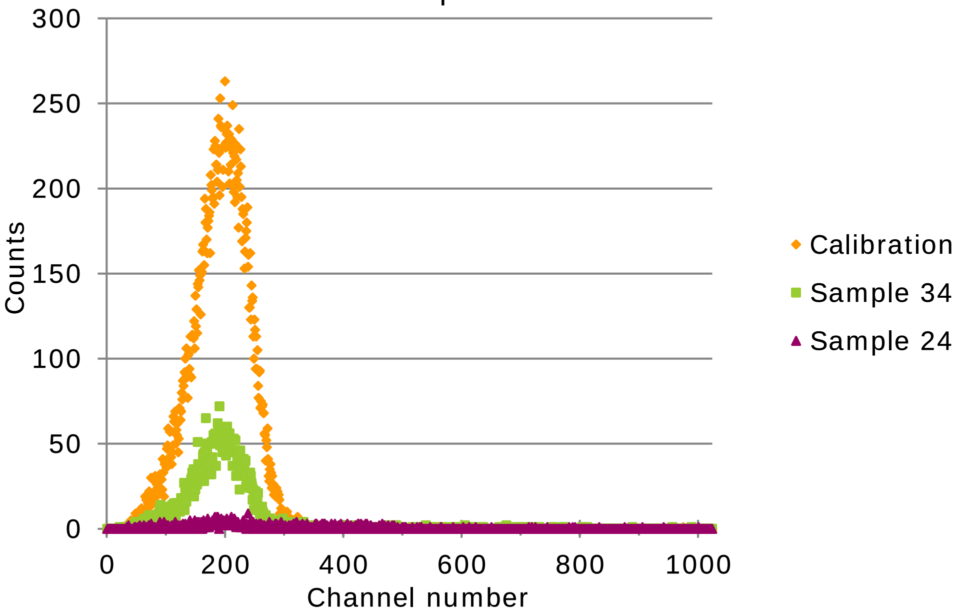
Measurement of ^{93}Mo using LSC

- Evaporated sample (300-400 µL) + 20 mL Ultima Gold LLT
- η = 52%

X-ray spectrum (HPGe)
Problem: self-absorption



LSC spectrum
Problem: quench



Method performance

- Recoveries:
  - Mo: typically over 85%
  - Nb: typically over 75%
  - Zr: typically over 70%

- The procedure was succesfully applied for the first 2 real samples

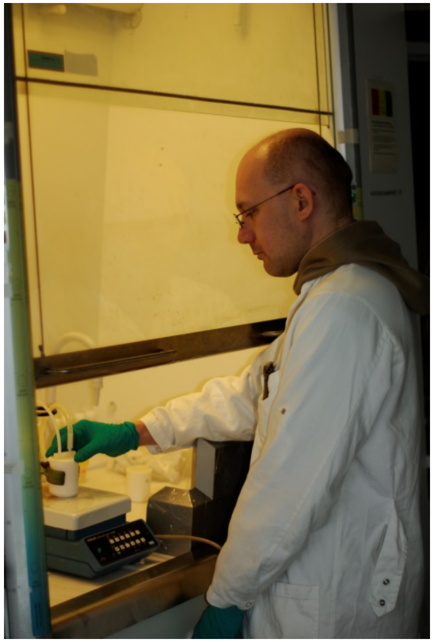
- Decontamination factors:

Separation of Mo			
Element	Cation exchange	TEVA Mo fr.	Alumina
Fe	$\geq 10^3$	10^3	$\geq 4*10^2$
Cr	≈ 2	500	$\geq 8*10^3$
Co	10^3	10^4	$\geq 10^2$
Ni	10^3	10^4	
Mn	10^3	10^4	
Nb	1	$5*10^2$	$\geq 2*10^4$
Zr	1	≥ 10	$\geq 7*10^2$
Sb	1		
Tc	1	$3*10^2$	$4*10^2$

Separation of Nb		
Element	Cation exchange	TEVA Nb fr.
Fe	$\geq 10^3$	10^5
Cr	≈ 2	10^3
Co	10^3	10^4
Ni	10^3	10^4
Mn	10^3	10^4
Mo	1	10^2
Zr	1	$\geq 10^2$
Sb	1	
Tc	1	10^3

Summary. Conclusions and perspectives

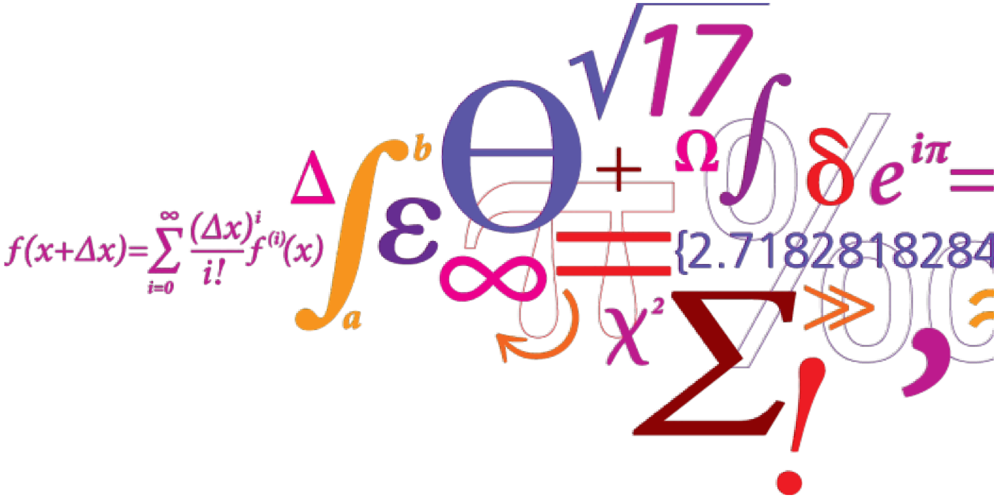
- A method for determination of ^{93}Mo (and ^{94}Nb) - based on combined chromatographic separation - was successfully developed
- Recoveries and separation factors are satisfying
- Analysis of real samples is in progress
  - Comparison of results with estimated values (based on modelling)
  - ^{125}Sb: need for an extra step?
- Validation by “standard addition” method
- Gamma-spectrometric measurement of ^{94}Nb before chemical separation (in the presence of lots of ^{60}Co) using an anti-coincidence gamma-spectrometer
- Method might be extended for determination of Zr (ICP: recovery, LSC: activity)



Thank you very much

for all your help and kind attention.

http://www.nutech.dtu.dk/english



We acquired the 3rd LSC spectrum in the world about ^{93}Mo

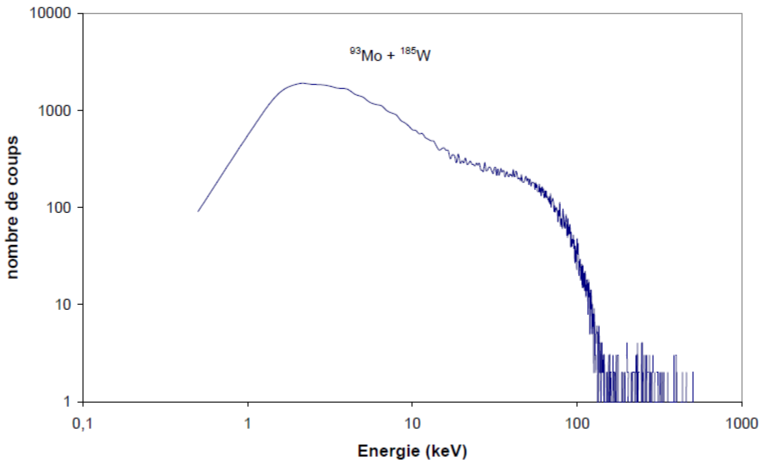
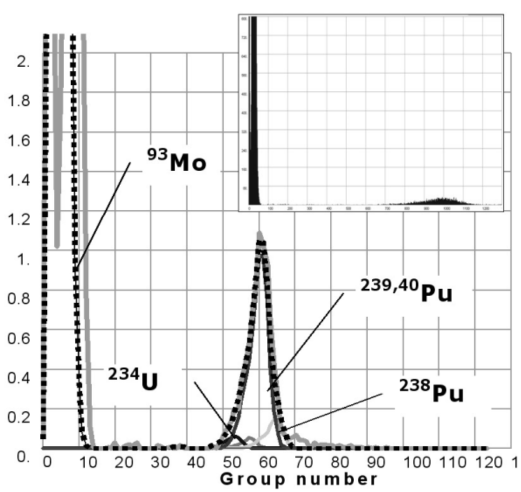


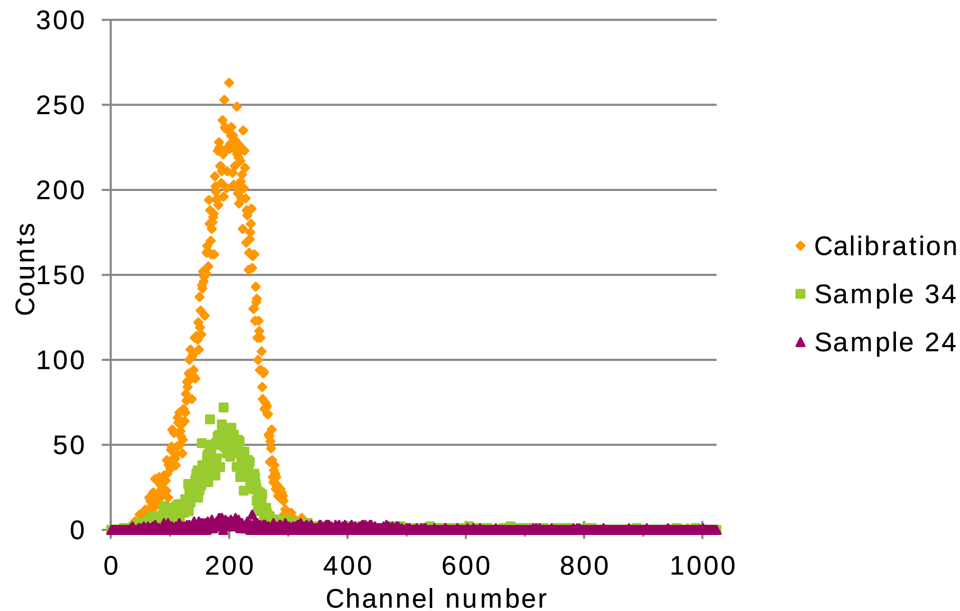
Figure 62 : Spectres de scintillation liquide de la fraction 202ME_M (temps de comptage = 600 minutes).

Reference:
Bombard (2005)
PhD Thesis,
Nantes University,
France (pp 139)

Contaminated with ^{185}W (433 keV, 100% β^-)



Reference:
Ermakov et al. (2005)
In: Chalupnik, Schönhofer, Noakes (eds):
LSC 2005, Advances in Liquid Scintillation Spectrometry (pp 89–98)



Calibration of LSC for measurement of ^{93}Mo

- No certified ^{93}Mo can be purchased
- "Home-made" solution: Separation of Mo from irradiated Nb
  - Dissolution and repeated evaporation: 40% HF + 68% HNO_3
  - Dissolution in 6 M HF
  - First separation step: Precipitation of Nb_2O_5 and co-precipitation on $Fe(OH)_3$ (using NH_3)

    Based on "the lost method" from Patricia Puech (1998): Détermination des radionucléides zirconium 93 et molybdène 93 dans des effluents de retraitement des combustibles irradiés. Thesis, Univ. Paris XI, 211, France
  - Repeated evaporation: 36% HCl + 68% HNO_3
  - Repeated evaporation: 40% HF
  - Dissolution in 0.1 M HF
  - Dilution until 0.05 M HF
  - Second separation step: purification on Alumina column
- Performance of separation: Recovery of Mo ≈ 60%

  DF of Nb $\geq 10^6$
- Measurement by calibrated X-ray spectrometer
- Measurement by LSC